

FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>Mueller-40</b>	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <b>10/030066</b>	
INTERNATIONAL APPLICATION NO. <b>PCT/DE00/02163</b>		INTERNATIONAL FILING DATE <b>6 July 2000</b>		PRIORITY DATE CLAIMED <b>7 July 1999</b>	
TITLE OF INVENTION <b>Method for Producing Metal Oxides Dispersibles in Organic Solvents [as amended]</b>					
APPLICANT(S) FOR DO/EO/US <b>Frank Michael Bohnen, Katja Siepen, Karen Reitz, and Paul K. Hurlburt</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.</li> <li>4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is attached hereto.</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input checked="" type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> <li>11. <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> </ol>					
Items 13 to 20 below concern document(s) or information included:					
<ol style="list-style-type: none"> <li>13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li>20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li>21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li>22. <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>23. <input checked="" type="checkbox"/> Other items or information: <b>Acknowledgment postcard</b></li> </ol>					



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
ACTING AS RECEIVING OFFICE FOR THE PCT

In re Application of:	§	Attorney Docket No.: Muller-40
	§	
Frank Michael Bohnen, Katja Siepen,	§	
Karen Reitz, and Paul K. Hurlburt	§	
	§	
Int'l. Appln. No.: PCT/DE00/02163	§	
	§	
Int'l. Filing Date: 6 July 2000	§	
	§	
Priority Date: 7 July 1999	§	
	§	
U.S. Serial No.: To Be Assigned	§	
	§	
U.S. Filing Date: Herewith	§	
	§	
For: <i>Method for Producing Metal Oxides</i>	§	
<i>Dispersibles in Organic Solvents</i>	§	
[as amended]	§	

**PRELIMINARY AMENDMENT**

Box PCT  
Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Kindly amend the above-identified application as follows:

**In the Specification**

On page 1, in lines 1-2, kindly delete the title and insert therefor the following new title:

METHOD FOR PRODUCING METAL OXIDES DISPERSIBLES  
IN ORGANIC SOLVENTS

On page 1, after the title and before line 5, please insert the following new heading and subheading:

**BACKGROUND OF THE INVENTION**

**FIELD OF THE INVENTION**

-2-

On page 1, at line 10, please insert the following new subheading:

DESCRIPTION OF THE PRIOR ART

On page 3, at line 33, please insert the following new heading:

SUMMARY OF THE INVENTION

On page 4, at line 8, please insert the following new heading and paragraph:

BRIEF DESCRIPTION OF THE DRAWINGS

The single figure is a graph showing viscosity versus time (days) of an acetone dispersion.

On page 4, at line 8, please insert the following new heading:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

**In the Claims**

Please cancel claims 1-17.

Please add the following new claims, 18-38:

NEWLY ADDED CLAIMS

18. (New) A process for preparing modified metal oxides or metal aquoxides that are dispersible in organic solvents comprising:
- (I) reacting
  - (A) at least metal oxide or metal aquoxide having a crystallite size of 4 to 100 nm, determined by x-ray diffraction on the 021 reflex, and a particle size of 5 to 500 nm, determined by photon correlation spectroscopy in dispersion.

-3-

with

- (B) at least one organic sulfonic acid wherein
    - (i) in case the reaction takes place in a mainly aqueous medium or in the absence of a diluent/solvent, the organic sulfonic acid is a mono-, di-, or trialkylbenzene sulfonic acid, wherein the alkyl residue(s) are C<sub>1</sub> to C<sub>6</sub> alkyl residue(s) and wherein the component (A), calculated as metal oxide, and (B) are used at weight ratios from 98:2 to 70:30, or
    - (ii) in case the reaction takes place in the presence of an organic aprotic solvent or an organic protic solvent, the organic sulfonic acid comprises at least 14 carbon atoms and at least one aromatic ring, and wherein the components (A), calculated as metal oxide, and (B) are used at weight ratios from 98:2 to 70:30, and
  - (II) drying the modified metal oxide or metal aquaoxide.
19. **(New)** The process according to claim 18, characterized in that said metal oxide or metal aquoxide contains aluminum.
20. **(New)** The process according to claim 19 wherein said metal oxide or metal aquoxide are selected from the group consisting of aluminas, alumina hydrates, aluminum silicate, Si/Al mixed oxides and mixtures thereof.

-4-

21. (New) The process according to claim 20 wherein said alumina hydrates are selected from the group consisting of boehmite, pseudoboehmite and mixtures thereof.
22. (New) The process according to any one of claims 18-21, characterized in that the organic sulfonic acid is a toluenesulfonic acid.
23. (New) The process according to claim 22 wherein said toluenesulfonic acid is p-toluenesulfonic acid.
24. (New) The process according to any one of claims 18-21, characterized in that the organic sulfonic acid has the formula  $R-SO_3H$ , wherein R is an alkyl-substituted aromatic hydrocarbon residue with 16 to 24 carbon atoms.
25. (New) The process according to any one of claims 18-21, characterized in that the metal oxides or metal aquoxides and the organic sulfonic acid are brought into contact at temperatures from 0 to 140°C.
26. (New) The process according to claim 25 wherein the temperature is from 0° to less than 90°C.
27. (New) The process according to any one of claims 18-21, characterized in that the metal oxides or metal aquoxides are brought into contact with the organic sulfonic acid for a period of time of from 30 seconds to 7 days.

-5-

28. (New) The process according to claim 27 wherein the period of time is from 30 to 90 minutes.
29. (New) The process of claim 27 conducted with stirring.
30. (New) The process according to any one of claims 18-21, characterized in that the modified metal oxides or metal aquoxides are dried by spray drying, freeze drying, microwave drying, drying in supercritical solvents, filtration, contact drying, or rotary drum drying.
31. (New) The process according to any one of claims 18-21, characterized in that the modified metal oxides or metal aquoxides are dispersed in organic solvent as dispersions having a solids content of 10 to 35 wt%.
32. (New) The process according to claim 31 wherein the solids content is from 20 to 30 weight percent.
33. (New) The process according to any one of claims 18-21, characterized in that the metal oxides or metal aquoxides are taken up in an organic solvent and this solvent is exchanged for a second solvent.

-6-

34. **(New)** The metal oxide or metal aquoxide dispersion comprising a metal oxide or metal aquoxide according to any one of claims 18-21, and a dispersant selected from the group consisting of
  - an aprotic polar organic solvent,
  - a protic, polar organic solvent having at least two carbon atoms,
  - an apolar organic solvent and mixtures thereof.
35. **(New)** The dispersion according to claim 34 wherein the dispersion contains an additive comprising at least one organic polymeric/oligomeric viscosity-adjusting agent.
36. **(New)** The dispersion according to claim 35 wherein the viscosity-adjusting agent is selected from the group consisting of cellulose, a cellulose derivative, a polyacrylate, a polyvinyl alcohol and mixtures thereof.
37. **(New)** The dispersion according to claim 36, characterized in that the dispersant is selected from the group consisting of a solvent-based paint, lacquer, a water-insoluble plastic, and mixtures thereof.



-7-

38. (New) A process according to any one of claims 18-21, characterized in that the modified metal oxides or metal aquoxides are processed into molded articles by extrusion, pelleting, or spherical drop forming processes.

Respectfully submitted,



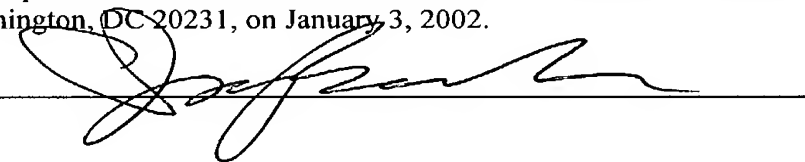
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**CERTIFICATE OF EXPRESS MAILING**

I, C. James Bushman, hereby certify that this correspondence and all referenced enclosures are being deposited by me with the United States Postal Service as Express Mail with Receipt No. EL715550119US in an envelope addressed to: Box PCT, Assistant Commissioner for Patents, Washington, DC 20231, on January 3, 2002.

By: 

Application as filed

1/p8h

10/030066  
JC13 Res'd PCT/PTO 03 JAN 2002

PROCESS FOR THE PREPARATION OF METAL OXIDES THAT ARE  
DISPERSIBLE IN ORGANIC SOLVENTS

- 5 This invention relates to a process for preparing metal  
oxides or metal aquoxides that are dispersible in organic  
solvents. The invention further relates to metal oxides  
or metal aquoxides that are modified with organic sul-  
fonic acids and can be prepared by this process.
- 10 From WO 95/12547 or German patent DE 43 37 643-C1, a pro-  
cess is known for the preparation of nanocrystalline alu-  
mina hydrates in boehmitic or pseudoboehmitic form that  
are dispersible in water. Water-dispersible alumina hy-  
15 drates can be obtained in this process by hydrolysis of  
aluminum alkoxides at temperatures from 30°C to 110°C,  
addition of an acid (monovalent inorganic or organic  
acids as well as their anhydrides), and subsequent hydro-  
thermal aging. The resultant suspensions are suitable for  
20 example for coating materials, such as glass, metal, or  
plastics, as well as for producing high-strength catalyst  
supports, pure-phase mixed oxides, or after conversion to  
the  $\alpha$ -form, for producing high-performance abrasives. The  
water-dispersibility of those alumina hydrates, which are  
25 not dispersible in organic solvents, is a disadvantage  
for certain applications, such as weather-resistant ex-  
terior coatings. For certain applications, aluminas that  
are dispersible in organic solvents but not in water are  
of interest.
- 30 The aluminas prepared by some of the processes known in  
the art are dispersible in dilute acids and water, and  
some of these aluminas are dispersible in short-chain  
alcohols, such as methanol and ethanol. They are not  
35 dispersible in organic aprotic solvents.

Application as filed

- 2 -

- Colloidal alumina solutions in organic solvents are described for example in DE 41 16 522-C2 as well as by R.
- 5 Naß and H. Schmidt ("Formation and Properties of Chelated Aluminum Alkoxides" in H. Hausner, G. Messing, S. Hirano (Eds.) "Ceramic Powder Processing", Deutsche Keramische Gesellschaft, Cologne, 1969). According to said publication, the alumina hydrates obtained by hydrolysis of alu-
- 10 minum alkoxides in an organic solvent and in the presence of a  $\beta$ -diketone compound can occur as colloids in the solvent. However, the colloidal solutions described there are only (meta)stable in the organic solvent at high dilutions. Only for isopropanol as a solvent has it been
- 15 experimentally proven that the solutions are in fact colloidal ones. Experiments have shown that after removal of the solvent, the colloidal particles prepared by said process cannot be redispersed.
- 20 From AU 200149 a process is known for the preparation of various inorganic oxides and hydroxides that can be dispersed in mineral oils. For this purpose, inorganic oxides or hydroxides are subjected to grinding in a ball mill in the presence of a surfactant and a mineral oil as
- 25 the carrier fluid. As surfactants, organic sulfonic acids are cited among others. The surfactants are added to the composition in quantities of 0.5 to 3 wt%.

- In US 3,018,172, a process is described for the prepara-
- 30 tion of aluminum hydroxides that are dispersible in non-polar, high-molecular organic solvents, such as mineral oils. In said process, aluminum alkoxides in a volatile organic solvent are hydrolyzed by contact with an organic sulfonic acid, such as postdodecylbenzenesulfonic acid in

**Application as filed**

- 3 -

a viscous organic carrier fluid. After hydrolysis, the volatile organic solvent is removed and an aluminum hydroxide dispersed in a viscous organic carrier fluid, such as xylene, remains.

A similar process is described in US 3,867,296, wherein a high-molecular organic sulfonic acid in a viscous organic carrier fluid is added to alumina hydrates in a volatile organic medium.

US 4,076,638 and US 4,123,231 describe variants of this process. According to US 4,076,638, a carboxylic acid is used in parallel, while the viscous organic carrier fluid is dispensed with. According to US 4,123,231, an aqueous mineral acid is used in addition to the organic sulfonic acid.

The processes described in the aforementioned U.S. patents have in common that substantial amounts of organic sulfonic acids must be used compared to the amount of alumina hydrate. In addition, organic solvents are required for the preparation of dispersible alumina.

According to AU 200149, mineral oxides are taken up in highly viscous mineral oils having a high solids content and then are dispersed in mineral spirits at high dilutions with a low solids content. However, these are no real colloidal solutions.

After drying, the products obtained by the aforesaid processes are no longer dispersible in organic solvents. It is the object of the present invention to provide dispersible metal oxides/metal aquoxides. It is a further

Application as filed

- 4 -

object of this invention to provide a process for preparing such products, which does not have the disadvantages of the prior art and, for example, does not require organic solvents for their preparation. These problems are solved by the subject matter of the invention.

The subject matter of the present invention is a process for preparing metal oxides or metal aquoxides, especially alumina hydrates that can be dispersed in protic or aprotic organic solvents. Said products can be obtained by reaction of

(A) one or a plurality of metal oxide(s)/metal aquoxide(s) having a crystallite size of 4 to 100 nm, preferably 6 to 20 nm (determined by x-ray diffraction on the 021 reflex) and a particle size of less than 1,000 nm, preferably 5 to 500 nm, most preferably 20 to 100 nm (determined by photon correlation spectroscopy (PCS) in the suspension prior to drying, for example during the production process)

(B) one or a plurality of organic sulfonic acid(s), where

(i) in case the reaction takes place in a largely aqueous medium or in the absence of a diluent, the organic sulfonic acid is a mono-, di-, or trialkylbenzene sulfonic acid, wherein the alkyl residue(s) is (are) C<sub>1</sub> to C<sub>6</sub> alkyl residues, preferably C<sub>1</sub> to C<sub>4</sub> alkyl residues, and mono-C<sub>1</sub>-alkylbenzene sulfonic acids or mono-C<sub>3</sub>-alkylbenzene sulfonic acids are preferred, or

ii) in case the reaction takes place in the presence of an organic aprotic solvent or an organic protic solvent, the organic sulfonic

Application as filed

- 5 -

acid has at least 14 carbon atoms, preferably at least 16, and at least one aromatic ring,

5 wherein the components (A), calculated as metal oxide, and (B) are used at weight ratios from 98:2 to 70:30, preferably from 95:5 to 80:20. Suitable organic protic solvents according to (ii) are for example alcohols, pre-  
10 ferably C<sub>2</sub> to C<sub>4</sub> alcohols. Suitable aprotic solvents according to (ii) are for example aromatic hydrocarbons, such as toluene. In case the reaction is carried out in the presence of a largely aqueous medium, it is preferred that the organic sulfonic acid be soluble in the largely  
15 aqueous medium.

Preferred embodiments are the subject matter of the sub-claims.

20 The solvents used as dispersants according to the invention are:  
(I) aprotic polar organic solvents  
(II) protic polar organic solvents having at least two carbon atoms, or  
25 (III) nonpolar organic solvents.

Suitable aprotic polar organic solvents (I) include ketones, ethers, and esters, such as acetone, tetrahydro-  
furan (THF), methyl ethyl ketone, polyol ester, 1,6-  
30 hexanedioldiacrylate, and dimethylsulfoxide (DMSO).

Suitable protic polar organic, optionally high-molecular, solvents (II) having at least two carbon atoms include alcohols, polyethers (with at least one free hydroxy  
35 group), hydroxyalkyl esters, and hydroxyalkyl ketones, or carboxylic acids. Suitable alcohols include for example

35 Part of the suspensions obtained in this way are trans-  
lucent. They produce transparent coatings, for example on

**Application as filed**

- 7 -

films/foils, glass, or similar surfaces. As a result of their dispersibility in organic solvents, the aluminas  
5 modified in this way are suitable for incorporation into various water-insoluble polymers or lacquers/paints.

Most of the suspensions prepared in this way are opaque. They are characterized by excellent sedimentation and  
10 centrifugation stabilities. Hence, they are genuine colloidal solutions. Another peculiarity is their redispersibility, especially after drying, in organic solvents, and the possibility of making stable suspensions with a high solids content (> 20 wt%). Surprisingly, the  
15 metal oxides/metal oxide hydrates obtained by the process of the present invention remain dispersible in the aforementioned dispersants (I) to (III), even after drying and, optionally, after finishing and/or storage.

20 In contrast to suspensions of alumina hydrates in aqueous systems, the viscosity increases only slightly at the beginning and then remains constant after one day (see Fig. 1/1). No sedimentation occurs, even not after several weeks. Owing to these properties, the p-toluenesulfonic  
25 acid-modified alumina hydrate of the invention is particularly easy to process and is most appropriate for making transparent coatings. Furthermore, it is useful as a filler in hydrophobic materials, such as PVC or lacquers/paints based on organic solvents.

30

**Dispersing Procedure**

Into a beaker, there were placed 18 grams of solvent and, while stirring vigorously, 2 grams of modified alumina  
35 hydrate were added in portions into the vortex within 1 to 5 minutes. The mixture was stirred for additional 10



## Application as filed

- 8 -

minutes. The resultant suspension had a solids content of 10 wt%. No sedimentation will occur with readily dispersible products. Dispersibility was determined by centrifugation of the suspension at 2,000 rpm (10 min), drying (at 120 °C), and weighing of the precipitate.

By the term 'dispersible metal oxides/metal aquoxides' employed herein especially those products are characterized which, when following the procedure described hereinbefore, remain in a dispersed state at  $\geq 95$  wt% or  $\geq 98$  wt%.

## 15 Example 1

20 grams of water-dispersible nanocrystalline alumina hydrate (crystallite size measured on the 120 reflex: 8-12 nm) (CONDEA product Disperal™ S), corresponding to 14.4 grams of  $\text{Al}_2\text{O}_3$ , were dispersed in a solution of 4 grams of p-toluenesulfonic acid in 180 grams of demineralized water and heated to 90°C for 30 minutes with stirring, thereby adjusting the pH-value to 1.5 and moderately thickening the suspension. After cooling, the suspension was spray dried (inlet temperature 240 to 270°C, outlet temperature  $< 110$  °C). A white odorless powder was obtained the properties and dispersibility of which are shown in Table 2 and Tables 1 and 4, respectively.

## 30 Example 2 (PTSA-Modified Silica Alumina)

Batch: 180 grams of demineralized water  
4 grams of p-toluenesulfonic acid (PTSA)  
20 grams of Siral™ 30 D

Application as filed

- 9 -

A suspension of 20 grams of Siral™ 30 D was prepared in a solution of 4 grams of *p*-toluenesulfonic acid in 180  
5 grams of demineralized water. The resultant yellowish sol-like suspension was spray dried. The C-value after drying was 8.61%. The powder was redispersible at 99% in water and ethanol. After solvent exchange, it was redispersible in hexanol and ethylene glycol, too.

10

### Example 3

4 grams of postdodecylbenzenesulfonic acid (Marlon™ AS-3) were dissolved in 180 grams of toluene. 20 grams of  
15 Disperal™ S were added. The mixture was stirred at 80°C for 30 minutes. The resultant yellowish sol with a solids content of approx. 10% contained aluminum oxide particles having a size of about 195 nm (measured by PCS). The sol was at 97.3% stable to centrifugation (10 minutes at  
20 2,000 rpm). After removal of the solvent at 40°C/77 mbar, a yellowish crystalline powder was obtained which was redispersible in toluene, tetrahydrofuran (THF), butanol, methyl-tert-butyl ether (MTBE), and trichloromethane. In chlorobenzene, a translucent suspension can be obtained,  
25 which is not stable to centrifugation, however. The powder is 100% hydrophobic, i.e., dispersibility in water was reduced to 0% by reaction with Marlon™ AS-3. The organosols are characterized by their long-term stability to agglomeration. No increase in viscosity was observed  
30 after several days. The dispersibility of the powder is shown in Table 3.

Application as filed

- 10 -

Table 1 Dispersibility in Various Organic Solvents

Solvent	Dispersibility (up to 10 wt% solids)	Particle Size [nm]	Transmission (0.1% solids) [%]	Remarks	Centrifugation Stability (2,000 rpm/10 min) [%]
Acetone	Yes (opaque)	80	60.6%	With 20% solids: thixotropic	84.2%
Ethanol	Yes	100	64.5%	-	99.0%
i-Propanol	Yes (limited)	-			Not determined
n-Butanol	Yes (opaque)	97			99.5%
Hexanol	Yes	335	65.8%	Thixotropic	84.6%
Ethyleneglycol	Yes (opaque)				
THF	Yes (opaque)	121			96.5%
DMSO	Yes (opaque)	104			95.0%
Chlorobenzene	By solvent exchange * (20% solids)	400		Low viscosity	99.5%
Dichloromethane	No	-			-
Toluene	By solvent exchange *	PCS not possible		Gelatinized	Not determined
1,6-Hexanediol- diacrylate	By solvent exchange *	-		Polymerized in UV	Not determined

5

\* At first dispersion in acetone, then addition of equal amounts of solvent (here: chlorobenzene), followed by displacement of the acetone by stirring with heating to 40 °C.

10

Table 2 Physical Characteristics of the Powder

		9.1 wt% PTSA	16.8 wt% PTSA
Specific surface area (BET) (activated for 3 h at 250 °C)	[ m <sup>2</sup> /g ]	-	135
Pore volume (0 - 1,000 nm pore diameter)	[ cm <sup>3</sup> /g ]	-	0.23
Average pore radius	[ nm ]	-	3.2
Al <sub>2</sub> O <sub>3</sub> content	[ % ]	-	66
C content	[ % ]	3.8	6.5
Particle size (dynamic laser scattering)		d <sub>10</sub> : 0.7 d <sub>50</sub> : 2.2 d <sub>90</sub> : 8.6	d <sub>10</sub> : 0.3 d <sub>50</sub> : 1.2 d <sub>90</sub> : 8.5

Application as filed

- 11 -

**Table 3 Dispersibility of Disperal™ S / Marlon™ AS-3 In Various Solvents**

Solvent	Dispersibility [ % ]	Particle Size (PCS) [ nm ]	Transmission [ % ]
Toluene	95.5	166	63.7
THF	99.0	113	32.3
Butanol	99.0	130	44.5
MTBE	85	-	6.8
Trichloromethane	98.5	64	42.3

5

**Table 4 Dispersibility of Disperal™ PTSA In Solvents Mixtures (10 wt% Solids)**

10

Solvent	Ratio	Particle Size (PCS) [ nm ]	Centrifugation Stability (2,000 rpm/10 min) [ % ]
CHCl <sub>3</sub> : MeOH	90 : 10	90	98
CHCl <sub>3</sub> : MeOH	70 : 30	70	97
CHCl <sub>3</sub> : MeOH	50 : 50	80	97.5
CHCl <sub>3</sub> : MeOH	30 : 70	107	97.5
CHCl <sub>3</sub> : MeOH	10 : 90	70	98.5
CH <sub>2</sub> Cl <sub>2</sub> : MeOH	90 : 10	97	98
CH <sub>2</sub> Cl <sub>2</sub> : MeOH	70 : 30	109	96
CH <sub>2</sub> Cl <sub>2</sub> : MeOH	50 : 50	103	96.3
CH <sub>2</sub> Cl <sub>2</sub> : MeOH	30 : 70	97	98.5
CHCl <sub>3</sub> : Acetone	70 : 30	148	84
CHCl <sub>3</sub> : Acetone	50 : 50	52	97.5

ART 34 AMDT

Claims as amended in PCT Chapter II proceedings

JC13 Res'd

PCT/PTO 03 JAN 2002

- 12 -

## Claims

1. A process for preparing modified metal oxides or  
5 metal aquoxides that are dispersible in organic  
solvents characterised by the following steps  
(I) by reaction of  
(A) one or a plurality of metal oxide(s) or metal  
10 aquoxide(s) having a crystallite size of 4 to  
100 nm, determined by x-ray diffraction on the  
021 reflex, and a particle size of 5 to 500 nm,  
determined by photon correlation spectroscopy  
in dispersion  
with  
15 (B) one or a plurality of organic sulfonic acid(s),  
where  
(i) in case the reaction takes place in a  
mainly aqueous medium or in the absence of  
a diluent/solvent, the organic sulfonic  
20 acid is a mono-, di-, or trialkylbenzene  
sulfonic acid, wherein the alkyl resi-  
due(s) are C<sub>1</sub> to C<sub>6</sub> alkyl residue(s) and  
wherein the component (A), calculated as  
metal oxide, and (B) are used at weight  
25 ratios from 98:2 to 70:30, or  
(ii) in case the reaction takes place in the  
presence of an organic aprotic solvent or  
an organic protic solvent, the organic  
sulfonic acid comprises at least 14 carbon  
30 atoms and at least one aromatic ring, and  
wherein the components (A), calculated as  
metal oxide, and (B) are used at weight  
ratios from 98:2 to 70:30.

## Claims as amended in PCT Chapter II proceedings

- 13 -

- (II) drying the modified metal oxides or metal  
5 aquaoxides, and  
(III) dispersing in organic solvents to get a  
dispersion
2. The process of claim 1,  
10 characterized in that as metal oxides or metal  
aquoxides, such metal oxides or metal aquoxides  
containing aluminium, preferably aluminas, alumina  
hydrates, particularly preferred boehmitic or  
pseudoboehmitic aluminas, aluminum silicate, or  
15 Si/Al mixed oxides are employed.
3. A process according to any one of the preceding  
claims,  
20 characterized in that the organic sulfonic acid is  
toluenesulfonic acid, preferably *p*-toluenesulfonic  
acid.
4. A process according to claim 1 or 2,  
25 characterized in that the organic sulfonic acid is  
an organic compound of the R-SO<sub>3</sub>H type, in which R  
is an alkyl-substituted aromatic hydrocarbon residue  
with 16 to 24 carbon atoms.
5. A process according to any one of the preceding  
30 claims,  
characterized in that the metal oxides or metal  
aquoxides and the organic sulfonic acid are brought  
into contact at temperatures from 0 to 140°C, pre-  
ferably from 0 to less than 90°C.

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- 14 -

6. A process according to any one of the preceding  
5 claims,  
characterized in that the metal oxides or metal  
aquoxides are brought into contact with the organic  
sulfonic acid for a period from 30 seconds to 7  
days, preferably from 30 to 90 minutes, and pre-  
10 ferably with stirring.
7. A process according to any one of the preceding  
claims,  
characterized in that the modified metal oxides or  
15 metal aquoxides are dried by spray drying, freeze  
drying, microwave drying, drying in supercritical  
solvents, filtration, contact drying, or rotary drum  
drying.
- 20 8. A process according to any one of the preceding  
claims,  
characterized in that the modified metal oxides/  
metal aquoxides are dispersible in organic solvent  
as dispersions having a solid content of 10 to 35  
25 wt%, preferably 20 to 30 wt%.
9. A process according to any one of the preceding  
claims,  
characterized in that the modified alumina hydrate  
30 is processed into molded articles by extrusion, pel-  
leting, or spherical drop forming processes.

## Claims as amended in PCT Chapter II proceedings

- 15 -

10. A process according to any one of the preceding claims,  
5 characterized in that the metal oxides or metal aquoxides are taken up in an organic solvent and this solvent is exchanged for a second solvent.
11. Metal oxide or metal aquoxide dispersion obtainable  
10 by the use of a dispersant and a metal oxide or metal aquoxide according to any one of the preceding claims, wherein the dispersant
- a aprotic polar organic solvents,
  - a protic, polar organic solvents having at least  
15 two carbon atoms, and/or
  - a apolar organic solvents.
12. Metal oxide or metal aquoxide dispersion of claim  
11,  
20 characterized in that the dispersion contains an additive of at least one organic polymeric/oligomeric viscosity-adjusting agent, preferably cellulose, a cellulose derivative, a poly-acrylate, or a polyvinyl alcohol.
- 25 13. Metal oxide or metal aquoxide dispersion of claim 11,  
characterized in that the dispersant is a solvent-based paint or lacquer or a water-insoluble  
30 plastics.



## Claims as amended in PCT Chapter II proceedings

- 16 -

14. Use of the metal oxides or metal aquoxides  
5       dispersions of claim 11 for preparing coatings,  
         preferably transparent coatings on foils,  
         metals/metal oxides, glass, PVC, and other plastics.
15. Use of the metal oxides or metal aquoxides  
10       dispersions of claim 11 for the production of  
         catalyst carrier.
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D-99805-UB+CA  


Abstract as filed

- 17 -

Abstract

5 The present invention relates to a process for preparing  
metal oxides or metal aquoxides, especially alumina hy-  
drates which can be dispersed in organic solvents, and to  
sulfonic acid-modified metal oxides or metal aquoxides  
that can be prepared by this process.

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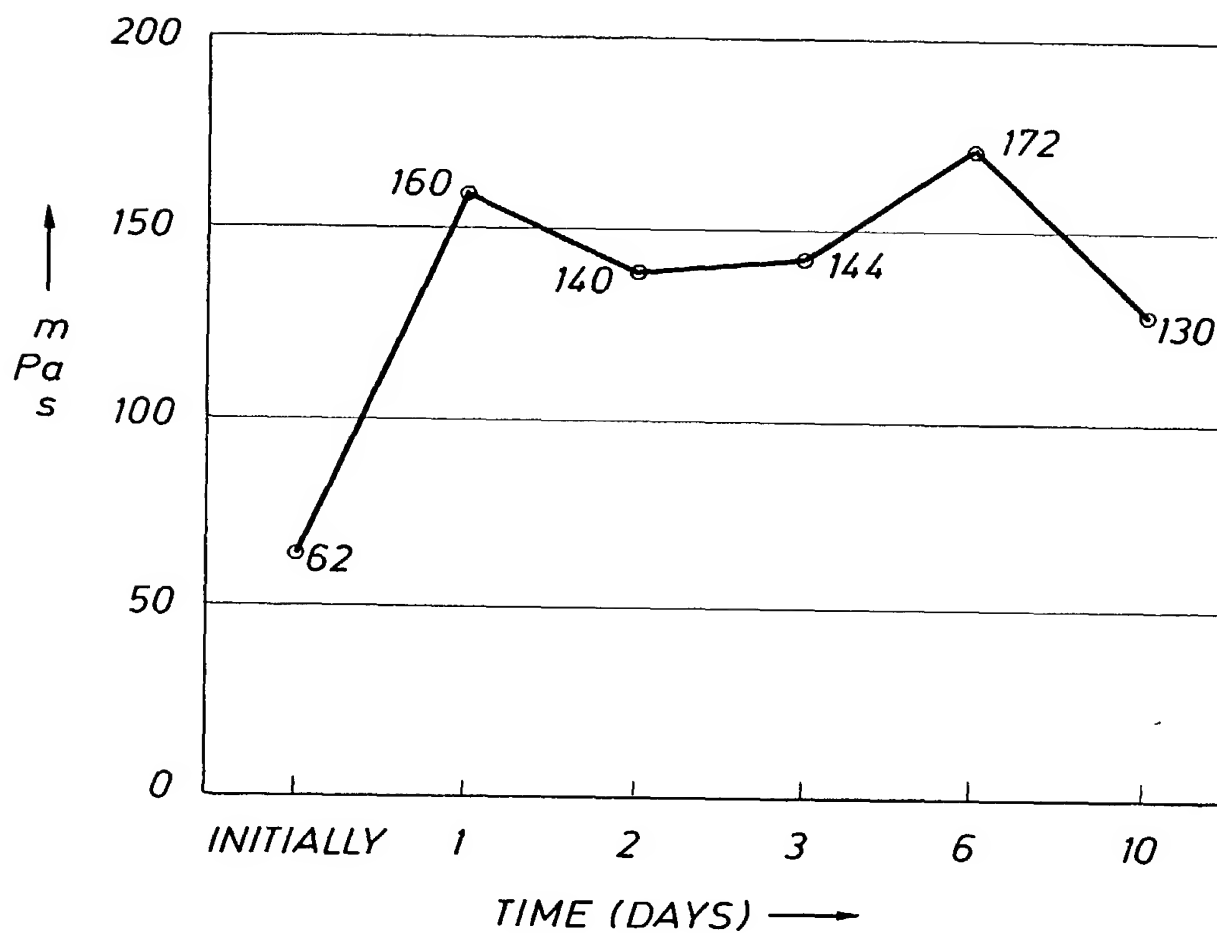
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Title: *Process for the Preparation of Metal Oxides that are Dispersible in Organic Solvents*  
Inventors: Frank Michael Bohnen, et al.  
U.S.S N.: To Be Assigned  
Atty: Docket No.: Muller-40  
Contact: C James Bushman, 713-266-5593

10/030066

1/1



Docket No.  
Mueller-40

# Declaration and Power of Attorney For Patent Application

## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled  
**Method for Producing Metal Oxides Dispersibles in Organic Solvents**

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on January 3, 2002 as United States Application No. or PCT International  
Application Number 10/030,066  
and was amended on \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)			Priority Not Claimed
<u>19931204.4</u>	<u>Germany</u>	<u>7 July 1999</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

**PCT/DE00/02163**

**6 July 2000**

**Pending**

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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